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Determination of dissociation energies of diatomic molecules from spectroscopic intensity measurements

The dissociation energies of CrO and MnO

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Abstract

The chemical equilibrium can be calculated from spectroscopic line intensity measurements and temperature measurements of an acetylene-air flame fed with a metallic salt solution. The dissociation energy of the metal oxide can then be determined from it. The dissociation energies of CrO and MnO were obtained in this way. The result is

$$D_{\mathrm{CrO}} = 4.4 \pm 0.5 \text{ e.v.}, \quad D_{\mathrm{MnO}} = 4.0 \pm 0.4 \text{ e.v.}$$

§ 1. Theoretical

A direct method for studying thermo-chemical equilibria, for instance the oxidation equilibrium at the absolute temperature T of a diatomic oxide

$$\mathrm{M} + \mathrm{O} \rightleftarrows \mathrm{MO}$$

consists in measuring the partial pressures p_{M}, p_{O} and p_{MO}. From the equation

$$\frac{p_{\mathrm{M}} \cdot p_{\mathrm{O}}}{p_{\mathrm{MO}}} = K_{\mathrm{MO}}(T) \tag{1}$$

one can obtain the equilibrium function $K_{\mathrm{MO}}(T)$. This function has the following form

$$K_{\mathrm{MO}}(T) = F(T) \cdot e^{-\frac{D}{kT}} \tag{2}$$

where D is the dissociation energy of the molecule MO. $F(T)$ contains atomic and molecular constants of the reaction components.

At moderate temperatures $K_{\mathrm{MO}}(T)$ depends mainly on the exponential factor $e^{-D/kT}$. Compared with the latter, $F(T)$ is very insensitive to variations both in T and in the constants. Thus, given $K_{\mathrm{MO}}(T)$ at a certain temperature, we can obtain the value of D, if it is possible to estimate the magnitude of $F(T)$. This will be discussed later.

If M is easily excited, its line spectrum is emitted at appropriate temperature. The intensity of a line in this spectrum is written

$$I = C N_{\mathrm{M}} A h \nu \frac{g e^{-E/kT}}{u(T)}, \tag{3}$$

where C is a space factor depending on the experimental conditions, N_{M} the number of atoms M, A the transition probability, h Planck's constant, ν the frequency of the line, g the statistical weight of the upper state and E its excitation energy. $u(T) = \sum g_i e^{-E_i/kT}$ is the partition function.

Putting

$$N_{\mathrm{M}} = p_{\mathrm{M}}/kT \tag{4}$$

it is evident from equ. (3) that p_{M} can be determined if I and T are measured and if C and the atomic constants in (3) are known.

The quantities ν, E_i and g_i are well-known from the analysis of atomic spectra. The space factor C can easily be determined. On the other hand, the absolute value of the transition probability A is known only for isolated lines of a few atoms.

Atomic oxygen does not emit any spectrum lines in the temperature region in question. Accordingly, it is impossible to determine p_{O} by the method described above. The same applies to p_{MO}, because, even if MO emits a band spectrum, the absolute transition probabilities for band lines are generally unknown. If, however, the total amounts of the element M and of oxygen in the light source are known, p_{O} and p_{MO} can be computed, as p_{M} is determined.

Using this method, we obtained the dissociation energies of the alkaline earth oxides (HULDT and LAGERQVIST, 1950). As a high temperature light source we used the acetylene-air-flame described by LUNDEGÅRDH (1929, 1934, 1936). A solution of a salt of the given element (M) is injected by means of compressed air into this flame.

The amounts of acetylene, air and solution entering the flame per second are very constant and reproducible and can easily be measured. The temperature was determined by spectrum line reversal, and the chemical equilibrium was calculated.

The method described requires a knowledge of the absolute transition probabilities A. In most cases, however, A is unknown. In such cases, it is possible to change the method in the following way by eliminating the factors A and C in equ. (3).

After measuring T and I by the above method, we decrease the temperature of the flame by feeding it with an excess of air. This new temperature is measured and also the corresponding line intensity. From (3) and (4) we obtain for the two different cases:

$$I' = C A \frac{h\nu}{kT'} p_{\mathrm{M}'} \, g \frac{e^{-E/kT'}}{u(T')}$$

$$I'' = C A \frac{h\nu}{kT''} p_{\mathrm{M}''} \, g \frac{e^{-E/kT''}}{u(T'')}$$

from which:

$$\frac{I'}{I''}=\frac{p_{\mathrm{M}'}}{p_{\mathrm{M}''}}\cdot\frac{T''}{T'}\,e^{\frac{E}{k}\left(\frac{1}{T''}-\frac{1}{T'}\right)}\,\frac{u(T'')}{u(T')} \tag{5}$$

where in most cases the factor $u(T')/u(T'')$ is practically $= 1$.

Thus, we avoid the use of the absolute line intensities and only need the quotient I'/I''.

Assuming M and MO to be the only components containing M, we may put

$$p_{\mathrm{M}}+p_{\mathrm{MO}}=\pi,$$

where π is determined from the known concentration of the solution. Equ. (1) then becomes

$$\frac{p_{\mathrm{M}}}{\pi-p_{\mathrm{M}}}=\frac{K_{\mathrm{MO}}(T)}{p_{\mathrm{O}}}$$

or (6)

$$p_{\mathrm{M}}=\frac{\pi}{1+p_{\mathrm{O}}/K_{\mathrm{MO}}(T)}.$$

From (6) for two different temperatures, we obtain the ratio

$$\frac{p_{\mathrm{M}'}}{p_{\mathrm{M}''}}=\frac{\pi'}{\pi''}\,\frac{1+p_{\mathrm{O}''}/K_{\mathrm{MO}}(T'')}{1+p_{\mathrm{O}'}/K_{\mathrm{MO}}(T')}. \tag{7}$$

In our case, $\pi'=\pi''$, as the concentration of the solution was unchanged.

From the measurements of the temperature and the intensity ratio I'/I'' we get from equ. (5) the value of $p_{\mathrm{M}'}/p_{\mathrm{M}''}$. Thus, the left hand member of (7) is found experimentally. Using equ. (2), the right hand side of (7) can be made to contain the dissociation energy D as the only unknown quantity. (The constants in the factor $F(T)$ can always be estimated with sufficient accuracy, as will be discussed later.)

When calculating the chemical equilibrium in the flame we consider in the first place only N_2 (inert), H_2, O_2, CO, CO_2, OH and H_2O. This leads to the following equations (HULDT 1948, p. 58):

$$\frac{p_{H_2}\sqrt{p_{O_2}}}{p_{\mathrm{H_2O}}}=K_1(T) \tag{8 a}$$

$$\frac{p_{\mathrm{OH}}\sqrt{p_{\mathrm{H_2}}}}{p_{\mathrm{H_2O}}}=K_2(T) \tag{8 b}$$

$$\frac{p_{\mathrm{CO}}\sqrt{p_{\mathrm{O_2}}}}{p_{\mathrm{CO_2}}}=K_3(T). \tag{8 c}$$

The equilibrium functions K_1, K_2 and K_3 are taken from ordinary chemical tables (JUSTI 1938, ZEISE 1942).

Besides equ. (8), four further equations exist, one for the total pressure and three expressing the composition of the flame. The amount of M is too small to be of any importance. From the pressure p_{O_2} thus calculated we get p_O from a similar equation:

$$\frac{p_O^2}{p_{O_2}} = K_4(T). \tag{8 d}$$

K_4 is given in Justi's tables.

The Brigg's logarithm of the function K_{MO} has the following form, when the pressures are in atm:s and D in electron volts:

$$\log K_{MO}(T) = -5040\frac{D}{T} + \frac{3}{2}\log T + \log\left(1 - e^{-hc\omega_e/kT}\right) + i_M + i_O - i_{MO} \tag{9}$$

where ω_e is the vibrational constant of the ground state in MO. Only the lowest electronic state is considered, but it is easy to correct for higher states, if such are known.

The chemical constants are calculated from

$$i_M = 1.587 + \frac{3}{2}\log \mathrm{M} + \log g_O \tag{10}$$

(M = atomic weight, g_O = statistical weight of the ground level).

$$i_{MO} = -1.738 + \frac{3}{2}\log(\mathrm{MO}) - \log B_O + \log g_O \tag{11}$$

(MO = molecular weight, B_O = rotational constant in cm^{-1} and g_O = the degree of degeneration in the ground level).

We see from (9), (10) and (11) that in the expression for $\log K_{MO}(T)$ all terms except the first one are logarithms. Errors in g_O, B_O and, still more, in ω_e have, therefore, very little importance for the magnitude of $\log K_{MO}(T)$. As will be shown later on, an alteration in g_O of a factor 6 is equivalent to a change of some tenths in D. This means that it is permissible to use roughly estimated values of the molecular constants mentioned.

§ 2. Experimental

The experiments were mainly performed in the same way as in our previous investigation (HULDT and LAGERQVIST 1950). The line intensities were measured photographic-photometrically. The plate was calibrated by means of a tungsten band lamp and by varying the slit width. The spectrograms were taken in a Hilger Medium Quartz Spectrograph. The densities were measured in a Stålex microphotometer. Corrections were made for the background density.

The line intensities were determined for each element at different concentrations of the solution in order to detect possible self-absorption. If self-absorption is present, the line intensity is not proportional to the concentration and equ. (3) and (5) are not fulfilled. The proportionality also shows that none of the metal compounds reached its saturated vapour pressure. If the pressure is saturated, the method cannot be used. This proportionality condition restricted considerably the choice of suitable elements, because it is also necessary for the exposures not to require too long a time (small concentrations). A number of elements are thus excluded at this stage, although they give strong lines in the flame. In this preliminary report we treat only the oxides of chromium and manganese.

The flame temperature was measured by reversal of the yellow sodium doublet and in some cases of the red lithium line too. As a continuous light source we used the tungsten band lamp, whose radiation temperature was measured with an optical pyrometer. From the tables of ZWIKKER (1925), VAN ALPHEN (1927) and HAMAKER (1934) it is then possible to correct the reading of the pyrometer. The amounts of acetylene, air and solution consumed per unit time were determined.

§ 3. **Results**

At ordinary running, the measured flame temperature was 2460° K. The composition of the flame gases was, according to the flow measurements:

$$C_2H_2 + 1.7\,O_2 + 6.4\,N_2 + 0.75\,H_2O,$$

which gives three equations for the relative abundance of the elements in the flame (see HULDT, 1948). Together with the condition for the total pressure and equ. (8), all these equations form a system from which we get the partial pressures.

On decreasing the supply of acetylene, the compcsition corresponds to the formula

$$C_2H_2 + 3.2\,O_2 + 12.0\,N_2 + 1.4\,H_2O$$

and the temperature was found to be 2110° K.

A thermo-chemical calculation of the theoretical flame temperatures gives sufficient agreement.

The solution has the same composition throughout the experiment:

$$MnSO\ (2.38 \times 10^{-4}\ \mathrm{mol/l}) + K_2Cr_2O_7\ (8.40 \times 10^{-3}\ \mathrm{mol/l}).$$

The observed lines were:

Mn:	4030.76 Å	$E = 24\,802\ \mathrm{cm}^{-1}$
Cr:	4289.72 Å	$23\,305\ \mathrm{cm}^{-1}$
	4274.80 Å	$23\,386\ \mathrm{cm}^{-1}$
	4254.35 Å	$23\,499\ \mathrm{cm}^{-1}$

The atomic data are taken from BACHER and GOUDSMIT (1932). The spectroscopic data for MnO and CrO are taken from HERZBERG (1950). No B-values are, however, obtainable. From different recursion formulas it is possible to estimate rough values for the internuclear distance r_e. These estimated r_e-values give B-values of the magnitude 0.4 for both oxides. As has already been mentioned such approximations do not influence the calculations.

Table 1 gives the experimental data. The line intensities are the means of two exposures. For Cr we have taken the mean of the three lines, as the Boltzmann factor is practically the same for them all.

Table 1

Temperature (in °K)	p_O (atm)	Line intensity for Mn	Line intensity for Cr
2460	$2 \cdot 3 \times 10^{-4}$	23	160
2110	$3 \cdot 3 \times 10^{-4}$	1	1

By inserting the data from Table 1 into equ. (7) we obtain the dissociation energies by trial and error. The nature of the electronic ground state of CrO and MnO is not definitely known, and, for this reason, the value of g_0 in (11) is not determined. The ground state of CrO may be a $^1\Sigma$, $^1\Pi$, $^3\Sigma$ or $^3\Pi$-state, which corresponds to $g_0 = 1$, 2, 3 and 6 respectively. Calculating D with each of these values we obtain 4.3, 4.4, 4.5 and 4.6 e.v. respectively. The uncertainty concerning the ground state thus has a very small influence upon D. For MnO the ground state may probably be $^2\Sigma\,(g_0 = 2)$ or $^2\Pi\,(g_0 = 4)$, corresponding to $D = 4.0$ and $D = 3.9$.

The error in the intensity measurements is negligible, because of the logarithmic connection. An error of a factor 2 in I'/I'' only means about 0.2 e.v. in D.

Errors in the determination of the composition of the gasous mixture are also of rather small importance. Thus, a change in the ratio acetylene/air of 20 % corresponds to an alteration in D of only 0.15 e.v.

The most serious source of error lies in the temperature determination. Under the present experimental conditions, the lower temperature has the greater influence upon the result. However, if the error in T'' is not greater than $\pm 50°$, the error in D is limited to about ± 0.2 e.v. The influence of the higher temperature is smaller ($\Delta D = \pm 0.1$ e.v. for $\Delta T' = \pm 100°$).

The D-values obtained here may be regarded as upper limits (Huldt and Lagerqvist 1950), because we have not considered the occurence of other metal compounds than the diatomic oxide. This assumption, however, seems to be very reasonable.

In conclusion we may give for the dissociation energy of CrO the value

$$D_{\mathrm{CrO}} = 4.4 \pm 0.5 \text{ e.v.}$$

and for MnO

$$D_{\mathrm{MnO}} = 4.0 \pm 0.4 \text{ e.v.}$$

Herzberg (1950) gives $D_{\mathrm{CrO}} = 3.8$ and $D_{\mathrm{MnO}} = 4.4$ e.v. and

Gaydon (1947) $D_{\mathrm{CrO}} = 3.2 \pm 0.5$ e.v. and $D_{\mathrm{MnO}} = 4.0 \pm 0.5$ e.v.[1]

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[1] Added in proof. Brewer and Mastick give $D_{\mathrm{MnO}} < 4.6$ e.v. (J. Chem. Phys., 1951, *19*, 834.)

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